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BEHAVIOR OF CARBON-14 ACTIVITY ON PARTICULATE SAMPLES FROM PICKERING NGS-A UNITS 1 AND 2 PART 1: SOLUBILITY IN SALINE AND DILUTE HCl SOLUTIONS

Report No 86-105-K

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ABSTRACT

The behavior of carbon-14 activity on various samples obtained during the retubing operation at Pickering NGS-A Units 1 and 2 was studied. Variable amounts of carbon-14 activity were extracted from particulate samples with saline solution and with hydrochloric acid (0.1 mol/L). The leachates were chemically classified by an acid distillation procedure.

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EXECUTIVE SUMMARY

BEHAVIOR OF CARBON-14 ACTIVITY ON PARTICULATE SAMPLES FROM PICKERING NGS-A UNITS 1 AND 2
PART 1: SOLUBILITY IN SALINE AND DILUTE HCl SOLUTIONS

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Carbon-14 is produced in the Pickering NGS-A annulus gas system (AGS) by the nuclear reaction N-14 (n,p) C-14. During normal operation most of the carbon-14 generated stays in the closed AGS, however,its fate has not been extensively studied. A relatively low energy of the beta particles of carbon-14 combined with very little gamma activity associated with the particulate material generated during the retubing operation made the survey and control of carbon-14 containing dust by conventional procedures difficult. Investigations were initiated because of the concern with the nature and behavior of the carbon-14 containing species. These included studies on the particle size distribution, filtration behavior, physical and chemical character and biologically important parameters such as solubility in simulated body fluids and some animal experiments for dose assignment purposes. This report summarizes some of the results obtained on the long term biological solubility in a saline solution (simulating lung fluid), 0.1 mol/L hydrochloric acid (simulating stomach fluid) and chemical characteristics of the species in solution.

Samples obtained from four different locations during the retubing operation were employed. These were airborne particulate material generated during shock heating operation, debris caught in the bellows and pigtails of the annulus gas system and contamination on some retubing tools. Leaching tests showed that there is an initial rapid dissolution of some of the carbon-14 activity containing species followed by a very slow increase in

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the leachate activity. Different samples showed a different solubility behavior indicating a varied composition of the material. The bulk of the activity (nearly 80%) remained unleached. The material showed a higher solubility in saline solution than in dilute hydrochloric acid. The leachate solutions were shown to contain 10 to 15 % inorganic, 40 to 60 % organic and 10 to 70 % relatively inert carbon-14 containing species.

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To
Dr. D. Mills
Director of Research

BEHAVIOR OF CARBON-14 ACTIVITY ON PARTICULATE SAMPLES
FROM PICKERING NGS-A UNITS 1 AND 2
PART I: SOLUBILITY IN SALINE AND DILUTE HCI SOLUTIONS

1.0 INTRODUCTION

An intense beta activity associated with the particulate material in the vaults of Units 1 and 2 of the Pickering NGS-A was discovered during the Large Scale Fuel Channel Replacement Project. The low energy of the beta radiation combined with very little gamma activity made survey and control of this loose contamination difficult by conventional procedures. Concern over the origin, nature and behavior of this activity resulted in an initial radioanalytical investigation which showed the material to contain large quantities of carbon-14.

The majority of the carbon-14 in the annulus gas system (AGS) is derived from the nitrogen gas in the system (N-14 (n,p) C-14). Video replay of the end fitting removal operation showed the probable cause of contamination in the vault area to be a black powder which was released as a fine dust. The loose black powder appeared to be concentrated mainly at the entrance or exit of the annulus gas into the core near the split end-fitting sleeve bearing. It was therefore assumed that the black powder was responsible for most of the mobile carbon-14 activity.

A large sampling and analysis program was carried out to determine particle size distribution, filtration behavior of particulate material and the distribution of activity as well as to collect material for further studies on the physical and chemical properties of the carbon-14 containing species /1,2/. This report presents results of some of the studies done on the above samples and some others made available later on during the retubing operation to characterize the chemical behavior of the carbon-14 containing species in the material.

2.0 LEACHING OF CARBON-14 ACTIVITY BY SALINE SOLUTION ND 0.1 MOL/L HCI

Preliminary studies on the mobility of carbon-14 activity on a dust sample obtained from the vault of Unit 1 of Pickering NGS-A were done at the request of Safety Services Department /3/. These studies, though not conclusive, showed that the carbon-14 containing species were not very soluble either in saline solution or in dilute HCl. The leach experiments were done over a period of 24 hours and in a batch mode. The need for data on long term biological solubility of the carbon-14 was required by Atomic Energy Control Board (AECB). The present set of experiments was designed to provide such data.

2.1 Experimental Procedures

2.1.1 Sample Description

Samples obtained from four different locations during the retubing operation were employed. These are airborne particulate material generated during shock heating operation, debris caught in the gas annulus bellows, material forced out of pigtails of the gas annulus system and contamination on some retubing tools. The sample descriptions and the test done on different samples are listed in Table I.

2.1.2 Leaching of Carbon-14 Activity by Saline-Solution

A sample containing approximately 0.2 to 5 uCi of carbon-14 activity was placed on an 0.1 micron Nucleopore polyester membrane filter mounted on a filter holder. A 12 micron membrane filter was placed on top and the system was sealed. Saline solution (0.154 mol/L NaCl with a pH of between 7 to 7.2) from a reservoir was circulated through the filter assembly at a rate of approximately 3 mL/minute. The experimental setup is shown in Figure 1.

After various intervals 1 mL aliquots were withdrawn from the reservoir and the carbon-14 content was determined by liquid scintillation counting. The activity in the leachate is considered to be the soluble fraction as it passed through an 0.1 micron filter. At the end of the leaching period (from 1 to 2 weeks) the filter assembly was dismantled and the carbon-14 activity on the filters was measured by liquid scintillation counting after burning the filters in a Packard TRI-CARB Sample Oxidizer. The total activity in the starting sample was determined by adding the residual activity on the filters and the

activity in the leachate. One of the experiments was terminated after less than two days of leaching due to a leak that developed in the filter assembly. The activity in this solution was measured and then it was filtered through a 0.1 micron filter. The activity of the filtrate was determined and was found to be the same as before filtration indicating no physical loss of the material from the filter to the solution.

TABLE I

Identification of Samples used in the Leaching Experiments

Sample Number	Sample Description	Leach Type	Information & Comments
1	Airborne particulate on Millipore filter from Shock Heating in Unit 2 in April/86	Saline	See /1,4/.
2	Airborne particulate on GF/E filter from Shock Heating of Channel H8 Unit 1 in May/86	Saline	See /1,4/.
3	Similar to Sample # 2 but from Channel G7 of Unit 1 in May/86	Saline	See /1,4/.
4	Similar to Sample # 3	Acid	
5	Subsample of debris from AGS bellows of Channel 13. September/86	Saline	See /4,5/.
6	Similar to Sample # 5	Acid	
7	Subsample of debris from Pigtails of AGS - Unit 1.	Saline	See /5/.
8	Similar to Sample # 7	Acid	
9	Active deposit on Calandria Tube Protective Sleeve Unit 2.	Saline	See /5/.
10	Similar to Sample # 10	Acid	

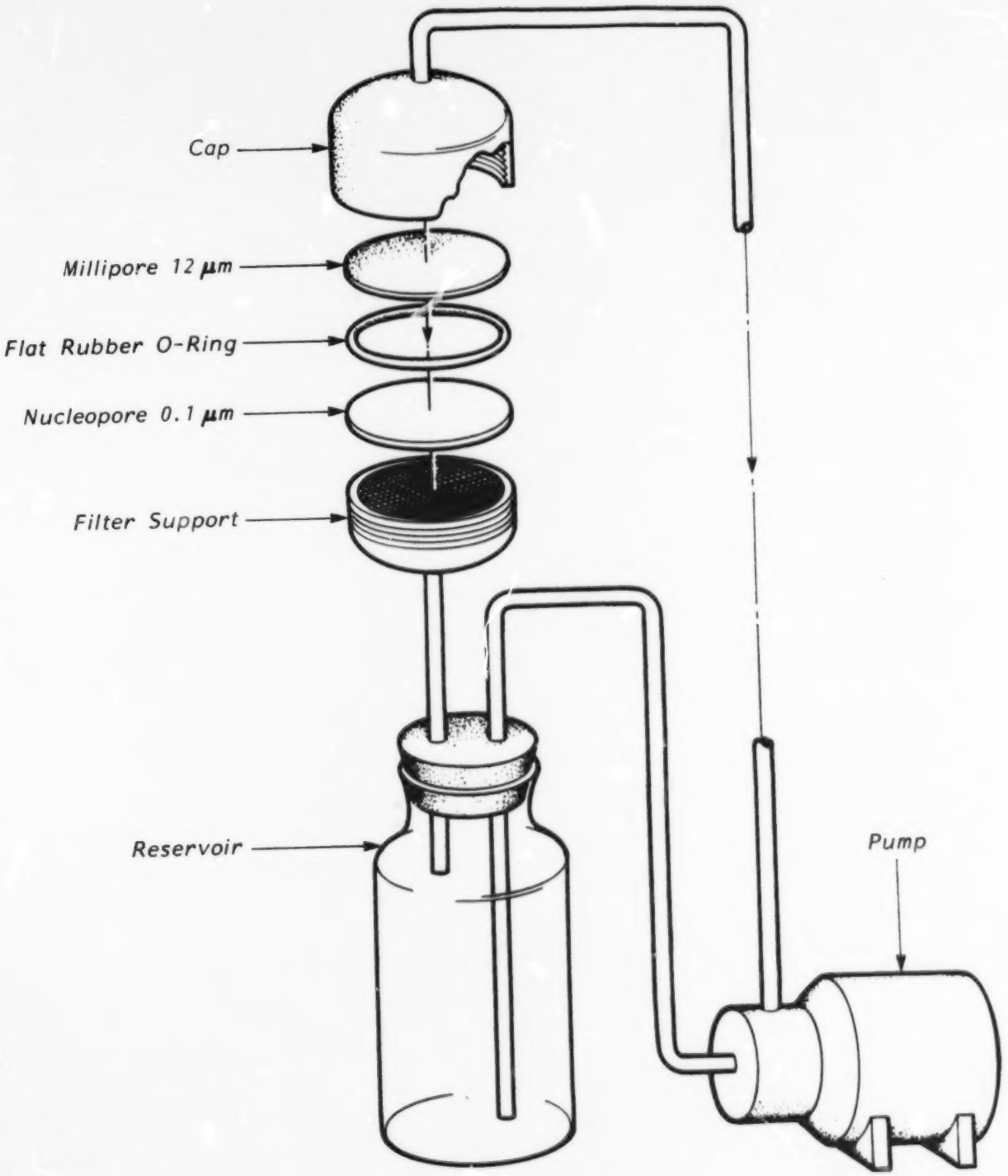

FIGURE 1

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2.1.3 Leaching of Carbon-14 Activity by 0.1 mol/L HCl

Leaching tests, similar to those described above with saline solution, were made with a fresh sample but using 0.1 mol/L hydrochloric acid instead of the saline solution. Because the system was exposed to the atmosphere during sampling any carbon-14 activity in the gaseous phase (produced by acid evolution of carbon dioxide) could escape. A separate experiment has shown that these losses are not significant.

2.2 Results and Discussion

2.2.1 Saline Leaching

There is an initial rapid dissolution of the soluble carbon-14 containing species followed by a very slow leach of relatively inert active material as shown by the data presented in Figure 2. However, there is a large variation in the total solubility of these species from sample to sample (nearly 3% to over 20%) as shown by the data in Table II. This variation in the total solubility could be attributed to different distribution of the various carbon-14 containing species in the samples. Physical examination and elemental analysis performed at Chemical Research has shown significant differences in the various samples, emphasizing the heterogeneous character of the material sampled from the reactor /4,5/. The observed variation in the leachability is therefore not surprising.

2.2.2 Acid Leaching

The leaching of carbon-14 containing species by 0.1 mol/L hydrochloric acid proceeds in a manner similar to that by saline solution. The results of the leaching experiments are shown in Figure 3. The total solubility of these species in acid solution varies from nearly 5% to under 15% as shown in Table III. The observed maximum total solubility in acidic solution (13%) is slightly lower than that in the saline solution (23%).

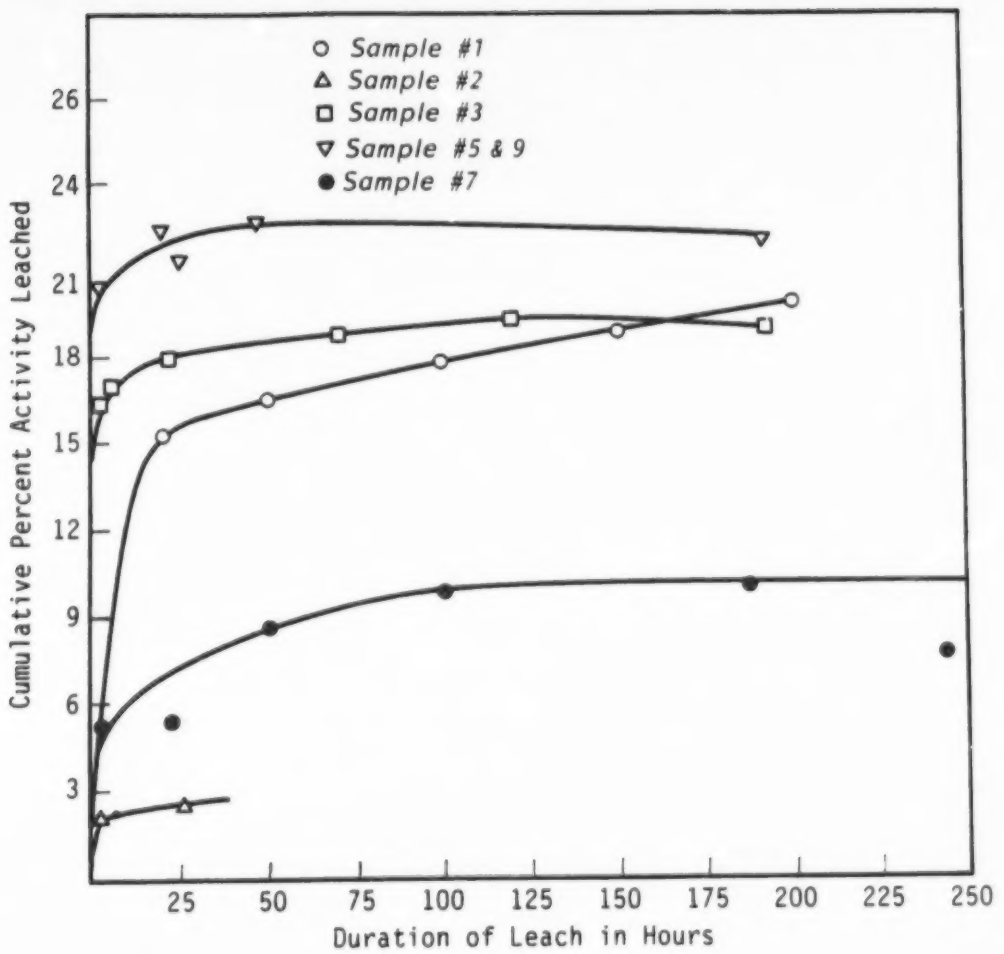
Sample #1
Sample #2
Sample #3
Sample #5 & 9
Sample #7
Cumulative Percent Activity Leached
26
24
21
18
15
12
9
6
3
25
50
75
100
125
150
175
200
225
250
Duration of Leach in Hours

FIGURE 2

TABLE II

Leaching Properties of theCarbon-14 Activityin Particulate Samples from Retubing Operation by Saline Solution

Sample Number	Initial Carbon-14 Act. (uCi)	Activity Leached out at termination of the Experiment. (%)	Comments
1	1.4	20	Sample on filter. Used as received.
2	4.5	2.5	Sample on filter. Used as received. Run terminated due to leak after 48 h
3	1.0	19.5	Sample on filter. Used as received.
5	0.2	23	Powder sample and a few specks used.
7	1.8	10	Powder sample and a few specks used.
9	1.0	23	Material of very high specific activity.

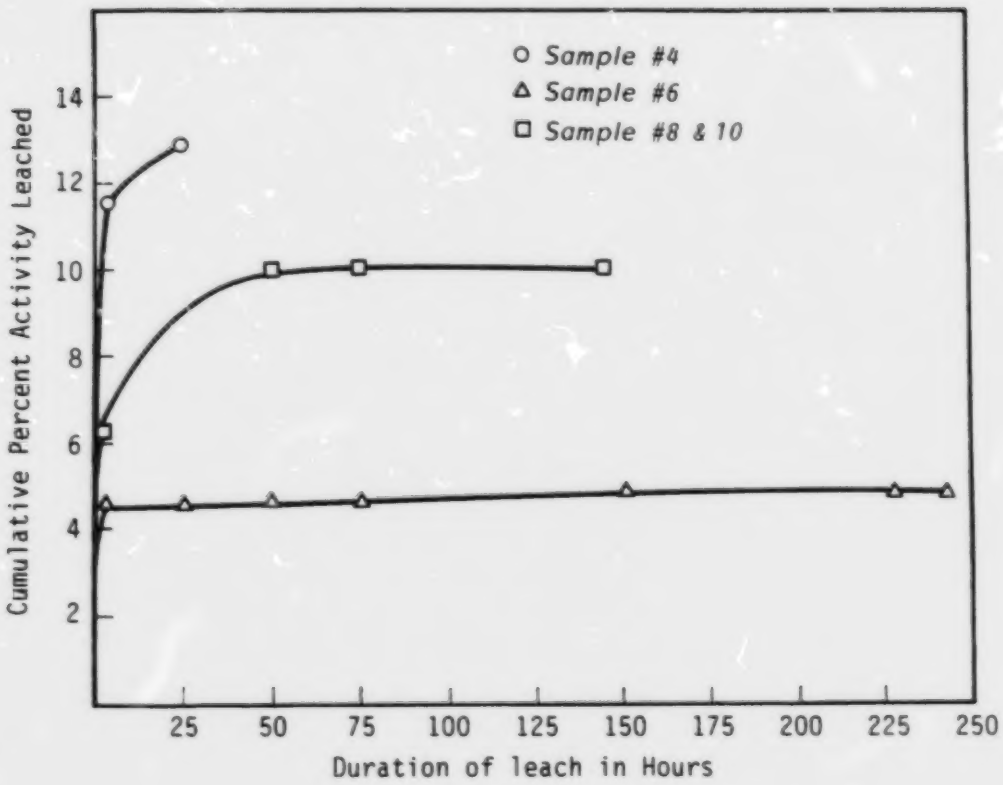
Sample #4
Sample #6
Sample #8 & 10
Cumulative Percent Activity Leached
14
12
10
8
6
4
2
25
50
75
100
125
150
175
200
225
250
Duration of leach in Hours

FIGURE 3

TABLE III

Leaching Properties of the Carbon-14 Activity in Particulate Samples from Retubing Operation by 0.1 mol/L HCl

Sample Number	Initial Carbon-14 Act. (uCi)	Activity Leached out at termination of the Experiment. (%)	Comments
4	1.1	13	Sample on filter. Used as received. Run terminated due to leak after 24 h
6	1.55	5	Powder sample and a few specks used.
8	1.6	10	Powder sample and a few specks used.
10	4.6	10	High specific activity material.

3.0 CHARACTERIZATION OF THE LEACHATES

The saline as well as the acidic leachates were characterized into three broad classes:

a) Inorganic forms
b) Organic forms
c) Unoxidizable and inert

The inorganic form of carbon-14 is defined to include all species which are either present or produced by the addition of acid and are low boiling and can be distilled from acidic medium. The organic forms are species which have been oxidized by persulphate ion to carbon dioxide. Unoxidizable residue may include inert forms of activity along with complex species which are not completely oxidized in the period of the experiment /6/.

3.1 Experimental Procedures

Briefly, the procedure involved sparging an acidified boiling leachate solution in a flask with air and trapping the resultant carbon dioxide and any other low boiling compounds in Carbosorb. The carbon-14 activity in the Carbosorb was measured by liquid

scintillation counting. This represents the inorganic fraction of carbon-14 containing species in the leachate solution.

The solution in the flask was cooled and a strong oxidant (potassium persulphate) and a catalyst (silver nitrate) were added. The solution was again brought to near boiling and sparged with air and the resultant carbon dioxide was trapped in a new portion of Carbosorb. The carbon-14 in the absorbent solution was measured by liquid scintillation counting to yield the organic fraction in the leachate. The unoxidizable fraction was calculated by difference.

3.2 Results and Discussion

The inorganic form content varied between 10 to 15 % of the total soluble activity, except for leachate from sample 7 which contained nearly 70 % and sample 6 containing 34 %. The experimental results are shown in Table IV for saline leachates and in Table V for acidic leachates. The organic content varied from 30 to over 60 % and unoxidizable forms from 10 to 60 %. These results clearly demonstrate that different samples contain variable amounts of many carbon-14 containing species.

TABLE IV

Chemical Characteristics of Saline Leachates

Sample Number	Carbon-14 Activity Present in Leachate in		
	Inorganic Form (%)	Organic Form (%)	Unoxidized (%)
1	12	45.5	42.5
3	14	62.5	23.5
5	14.5	41	44.5
7	69	19	12
9	6	31	63

TABLE V

Chemical Characteristics of Acidic Leachates

Sample Number	Carbon-14 Activity Present in Leachate in: Inorganic Form (%)	Organic Form (%)	Unoxidized (%)
6	34	36	30
8	6	33.5	60.5
10	6	49	45

4.0 PRESENCE OF OTHER LONG LIVED PURE LOW ENERGY BETA EMITTERS AND THEIR SIGNIFICANCE IN LEACHING EXPERIMENTS

There have been discussions about other pure low energy beta emitters which could be present in the AGS. It has been proposed that zirconium-93 (Zr-92 (n,γ) Zr-93) and nickel-63 (Ni-62 (n,γ) Ni-63) may be contributing to the activity in the particulate material in the annulus gas system /7,8/. Of these, nickel-63 could be leached out during these experiments. This could alter the estimation of exposure to carbon-14 and subsequent dose assignment /9/.

Nickel is present in the zircaloy tubes to an extent of 0.05 %. Nickel-62 has a natural abundance of 3.6 % and has a thermal neutron capture cross section of 14.2 barns. Zirconium-92 has a natural abundance of 17.1 % and a thermal capture cross section of 0.2 barns compared to 17.5 % natural abundance and 0.055 barns capture cross section for zirconium-94. Zirconium has not been found to be a major component of any of the samples investigated in this study, though traces of zircaloy may be present /5/. In the absence of a significant enrichment of any of these radionuclides in the particulate samples under investigation, an estimate of the ratio of activities of these pure beta emitters to that of zirconium-95 can be made and are listed in Appendix. The activity of zirconium-95 is order of magnitude greater than that of zirconium-93 or nickel-63 for cooling period of 1 to 2 years.

Very little zirconium-95 activity was observed in the gamma scans of the samples used in the present study and it was concluded that both zirconium-93 and nickel-63 do not make any significant contribution to the total activity of the samples. The leaching

experiments show the leachability of carbon-14 containing species only and very little if any contribution is made by other radionuclides.

5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 The leachability of carbon-14 containing species by saline solution as well as 0.1 mol/L hydrochloric acid from four types of particulate sample was studied. An initial large rate of dissolution was followed by a very slow leach of carbon-14 containing species. Most of the leachable fraction of the activity dissolves with in a period of 50 hours.

5.2 Only a small fraction of the carbon-14 containing material seems to be soluble. The majority of the material (nearly 80 %) appears to be quite inert.

5.3 The total solubility of carbon-14 containing species in saline solution was observed to be slightly higher than that in dilute acid. Different solubility was observed for different samples both in the saline as well as in the acidic medium. This reflects the heterogeneity of the samples under investigation.

5.4 The leachates were analyzed for gross character of the carbon-14 containing species by a distillation process. Three categories were defined as:

Inorganic (including low boiling organics which could be distilled out of an acid medium).

Organics (defined as oxidizable by aqueous persulphate ion).

Unoxidizable.

The proportion of these fractions in the leachate also showed variation from one sample to another. This indicates the presence of variable concentrations of diverse chemical species. No attempt was made to chemically identify individual species in the alkaline or acidic leachate solutions.

5.5 Radionuclide other than carbon-14 do not contribute significantly to the total activity of the samples under investigation. The leaching experiments demonstrate the leachability of carbon-14 containing species.

The exact chemical nature of the species would be quite helpful in predicting the behavior of the carbon-14 contamination. Some attempts in this direction have been made and will be the subject of future reports from Chemical Research. The nature of material deposited on the tube and not mobilized and hence not sampled and studied would also help in understanding the chemistry of the deposition and would throw light on the very nature of the carbon-14 containing species.

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APPENDIX

Estimation of the Activity Ratios Zr-93/Zr-95 and Ni-63/Zr-95

Activity (A) of a radionuclide produced in a reactor is given by:

$$A = N\sigma\Phi \quad (1-EXP(-\lambda T_i))$$

where

- N is the number of target nuclei
- σ is the nuclear reaction cross section
- Φ is the neutron flux in the reactor
- λ is the decay constant of the product nuclide
- T_i is the time of irradiation

Saturation activity (A_s) is given by:

$$A_s = N\sigma\Phi$$

Assuming that the reactor has operated long enough to produce saturation activity of Zr-95 (nearly a year), the activity ratio Zr-93/Zr-95 and Ni-63/Zr-95 can be calculated as follows:

$$\text{Zr-93/Zr-95} = 3.57 \times \text{Exp}\,(3.86 \times T_c) \times \frac{(1-\text{Exp}\,(-6.93\ \text{E-07} \times T_i))}{(1-\text{Exp}\,(-3.86 \times T_i))}$$

and

$$\text{Ni-63/Zr-95} = 0.041 \times \text{Exp}\,(3.86 \times T_c) \times \frac{(1-\text{Exp}\,(-0.0075 \times T_i))}{(1-\text{Exp}\,(-3.86 \times T_i))}$$

Where

T_c is the cooling period in years.

These ratios have been calculated for different irradiation and cooling periods and are listed in Tables AI and AII. These calculated ratios can be used to get an approximate magnitude of the concentration of two radionuclides provided zirconium-95 activity could be determined by gamma spectroscopy.

TABLE AI

Variation in the Zr-93/Zr-95 Activity Ratio with Different Irradiation Times and Cooling Periods

Irradiation Time (Years)	Zr-93/Zr-95 Activity Ratio after a Cooling Period of (Y)				
	0	1	2	3	4
1	2.47E-6	1.17E-4	5.56E-3	0.264	12.5
5	1.24E-5	5.86E-4	2.87E-2	1.32	62.7
10	2.47E-5	1.17E-4	5.56E-2	2.64	125

TABLE AII

Variation in the Ni-63/Zr-95 Activity Ratio with Different Irradiation Times and Cooling Periods

Irradiation Time (Years)	Ni-63/Zr-95 Activity Ratio after a Cooling Period of (Y)				
	0	1	2	3	4
1	3.08E-4	1.46E-2	0.693	32.9	1562
5	1.51E-3	7.17E-2	3.40	167	7927
10	2.96E-3	0.140	6.67	376	17847

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